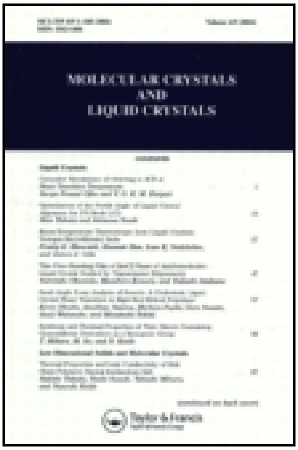

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Raman Scattering and X-Ray Diffraction Studies on Alkali-Metal Intercalated Clays

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Vermiculite and fluor-tetrasilicic mica were intercalated with alkali metals (Na, K and Rb) by vapor transport. X-ray and Raman scattering experiments were conducted to study the structure and lattice dynamics of the new clay compounds. When Rb and K atoms were intercalated to the host materials, superlattices were formed. In Na intercalated compounds, however, no superlattice x-ray diffraction peaks were found. Raman spectra exhibited drastic changes after alkali-metal intercalation, reflecting the structural changes found by our x-ray diffraction.

Keywords: vermiculite; fluor-tetrasilicic mica; alkali-metal intercalation; x-ray diffraction; Raman scattering; neutron scattering

INTRODUCTION

Clay minerals (layered silicates) have attracted many researchers for many decades because of their interesting physical properties. Especially, their ability to accommodate many foreign guest species between host silicate layers provides stimulative opportunities for the intercalation physics and chemistry.

Recently, we have found that layered silicates such as vermiculite and artificial fluor-tetrasilicic mica could be intercalated with alkali metals (Na, K and Rb) by a vapor-transport method in an evacuated glass tube using a two-temperature zone furnace [1,2]. It was found that the electrical conductivity increased drastically upon intercalation. Rb-intercalated vermiculite, for example, exhibited an energy-activation-type temperature dependence with $E_a \sim 0.1$ eV. X-ray fluorescence analyses yielded that a Rb-intercalated vermiculite single-crystal could contain as much as 40 percent more Rb atoms than the original Rb cation-exchanged sample. Also known was the fact that, from SQUID magnetic measurements, the number of Curie free spins decreased upon alkali-atom intercalation but the temperature-independent paramagnetic susceptibility contribution increased after alkali-metal intercalation [2].

EXPERIMENTAL

For single crystal studies, Llano vermiculite of which chemical composition was approximately $Mg_{0.93}(Mg_{5.58}Al_{0.10}Fe_{0.03}Ti_{0.02})^{oct}(Si_{5.72}Al_{2.28})^{tet}O_{20}(OH)_4$ [3] was used. For powder studies, synthetic fluor-tetrasilicic mica (fluor mica) from Co-op Chemical Co., LTD was used. The ideal chemical composition for F-mica is $Na_{0.64}(Mg_{2.68}◎_{0.32})^{oct}(Si_4)^{tet}O_{10}F_2$ [4], where ◎ stands for a vacancy. Both samples contain one octahedral sheet sandwiched with two tetrahedral sheets, and are classified as 2:1 clay minerals. Samples were first cation-exchanged, then were dehydrated in vacuum, and were finally heated in an evacuated glass tube with a desired intercalant metal in a two-temperature-zone furnace.

X-ray diffraction measurements were conducted with a four-circle diffractometer using the Mo $K\alpha_1$ and $K\alpha_2$ lines. Raman spectra were taken using a liquid-nitrogen cooled CCD detector and an Ar-ion laser ($\lambda = 5145$ Å).

RESULTS AND DISCUSSIONS

Figure 1 shows an $(0\,0\,\ell)$ out-of-plane x-ray diffraction patterns taken from Rb cation-exchanged (i.e., the interlamellar cations are Rb^+) and Rb intercalated vermiculite samples at room temperature. The Bragg peaks from the cation-exchanged vermiculite yielded the basal spacing to be 10.35 ±0.02 Å. After Rb intercalation, the basal spacing did not seem to change noticeably, but the peaks might become broader upon intercalation. Also notice that there appeared new Bragg peaks as indicated in the figure by the arrow marks. We speculate that these new Bragg peaks might correspond to a new basal spacing of which the repeat distance is

~11.32 Å. If one assumes that the intercalated Rb ions sit on the triads of oxygen atoms instead of the pseudo-hexagonal holes in the host layer, one can approximately reduce the repeat distance of that value (11.3 Å) from the known radii of Rb^+ and oxygen atoms. Considering the amount of intercalated Rb atoms (as much as 40 %), our interpretation of the new Bragg peaks might be plausible.

Figure 2 depicts (*h* 0 0) x-ray diffraction patterns from the Rb cation-exchanged and Rb intercalated vermiculites. New Bragg peaks again appeared after the intercalation process. Since these peaks do not correspond to a simple

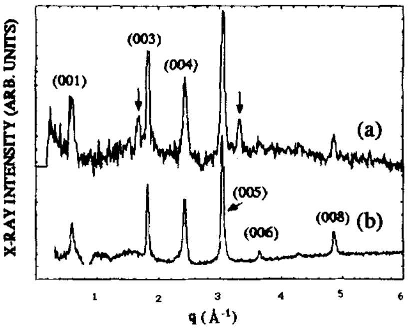

FIGURE 1 (0 0 ℓ) x-ray diffraction patterns taken from (a) Rb intercalated vermiculite and (b) Rb cation-exchanged vermiculite. Diffuse diffraction intensities from a glass ampule were subtracted. The arrows in (a) indicates new Bragg peaks.

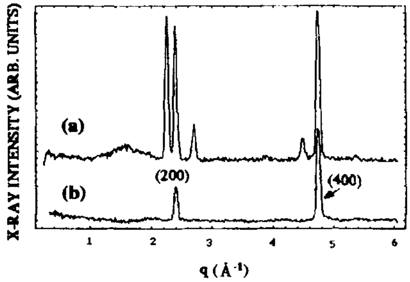

FIGURE 2 (*h* 0 0) x-ray diffraction patterns taken from (a) Rb intercalated vermiculite and (b) Rb cation-exchanged vermiculite. Diffuse diffraction intensities from a glass ampule were subtracted.

commensurate superlattice peaks, we may conclude that there may be a new incommensurate superlattice formed upon intercalation. The reason why the new Bragg peaks are so pronounced is that a Rb atom contains much more electrons than those other atoms in the crystal. It is mentioned that (0 *k* 0) diffraction patterns also showed new Bragg peaks corresponding to the new superlattice. It was found that K intercalated vermiculite also exhibited superlattice diffraction patterns with different lattice constants from those of Rb vermiculite [5].

Figure 3 shows powder x-ray diffraction patterns taken from Na fluor-tetrasilicic mica samples together with an x-ray diffraction pattern of Rb cation-exchanged fluor mica for comparison. It can be noticed that the diffraction pattern of Na fluor mica did not change much after Na intercalation. The only noticeable differences are that (1) the Bragg peak widths may have become somewhat broadened and (2) some peaks may have shifted slightly by intercalation. In Rb fluor mica, new superlattice peaks appeared [5] as in the case of Rb vermiculite as discussed above. Note that in Na vermiculite, no superlattice Bragg peaks were observed after Na intercalation but the in-plane *a* and *b* lattice constants became larger by ~1% after intercalation [5].

Raman spectra were taken from Rb vermiculite and are shown in Fig. 4. From the figure, one notices that the Raman peak at 195 cm^{-1} in Spectrum (c) downshifted by ~5 cm^{-1} and became broader slightly after Rb intercalation. The peaks at ~355 and 680 cm^{-1} became somehow indistinguishable. Similar trends

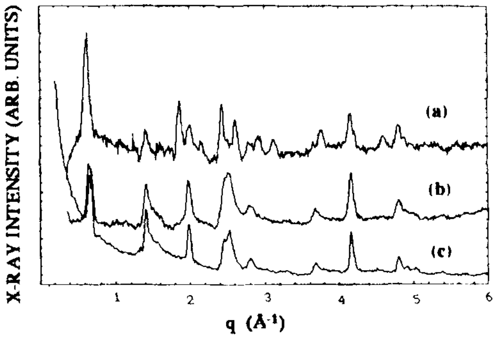

FIGURE 3 Powder x-ray diffraction patterns taken at room temperature from (a) Rb cation-exchanged fluor mica, (b) Na intercalated fluor mica, and (c) Na cation-exchanged fluor mica. Diffuse diffraction intensities from a glass ampule were subtracted.

were found in the Raman spectrum of K intercalated vermiculite [2].

Figure 5 shows Raman spectra taken from Na fluor mica samples and a spectrum of as-is Na vermiculite. The spectra, (c) and (d) were taken from the same powder sample in the same ampule; the spectrum (d) was taken from the part more extensively exposed to a Na vapor during the intercalation process. We do not think that the Raman peak at ~200 cm^{-1} in Spectrum (d) should originate

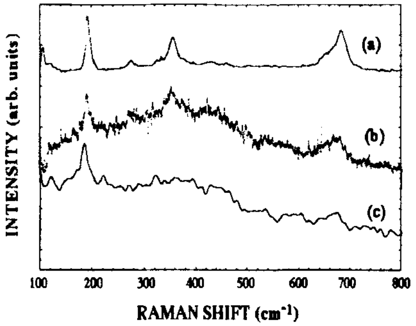

FIGURE 4 Raman spectra taken at room temperature from (a) as-is (not dehydrated) Rb cation-exchanged vermiculite, (b) dehydrated Rb cation-exchanged vermiculite, and (c) Rb intercalated vermiculite. Spectra (b) and (c) were obtained after subtracting Raman scattering intensities from a glass ampule.

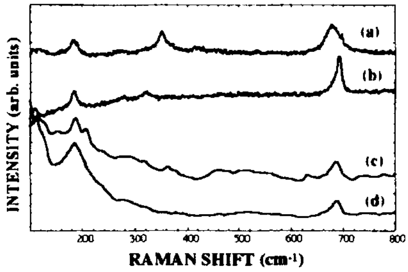

FIGURE 5 Raman spectra taken at room temperature from (a) as-is (not dehydrated) Na cation-exchanged vermiculite, (b) as-is Na cation-exchanged fluor mica, (c) Na intercalated fluor mica, and (d) Na intercalated fluor mica. Spectra (c) and (d) were taken from different spots of the same powder. Spectra (b), (c) and (d) were obtained after subtracting Raman scattering intensities from a glass ampule.

from Na_2O, because the sample had never been immersed in Na metal in the evacuated ampule (i.e., it is unlikely that Na_2O was made near the sample). Thus, we conclude that the Na intercalant atoms drastically affected the surface oxygen vibrational mode at 200 cm^{-1} [6]. This drastic change in the Raman spectrum may be related to the in-plane expansion of the host layer upon Na intercalation as mentioned above.

CONCLUDING REMARKS

Our x-ray and Raman scattering experiments showed that 2:1 layered silicates could undoubtedly accommodate alkali atoms in the gallery between the host silicate layers. It was found that the structures and lattice dynamics strongly depended on what kind of alkali atoms the intercalant atoms were (the radius of atom should be a crucial parameter), and did not probably depend much on what kind of layered silicates examined (the interlamellar intercalant atoms are just sandwiched by flat oxygen layers in any cases).

Our experimental results suggest that the alkali-metal intercalated clay systems may provide a new playground for the intercalation physics. In particular, understanding the mechanism for the quasi-2D electrical conduction should be of great interest.

Acknowledgments

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